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(54) HONEYCOMB STRUCTURE AND METHOD FOR MANUFACTURE THEREOF

(57) A honeycomb structure having, in the axial direction, a number of through-channels separated by partition walls, which honeycomb structure contains refractory particles and a vitreous component and is porous. Although the honeycomb structure contains re-

fractory particles such as silicon carbide particles or the like, it can be produced at a relatively low firing temperature; therefore, the honeycomb structure has a low production cost and a high yield and can be provided at a low price.

EP 1 170 270 A1

Description

Technical Field

- 5 [0001] The present invention relates to a honeycomb structure used in a filter for purification of automobile exhaust gas, a catalyst carrier, or the like.

Background Art

- 10 [0002] Porous honeycomb structures are in wide use as a filter for capturing and removing the particulate substance present in a dust-containing fluid (e.g. exhaust gas emitted from diesel engine) or as a catalyst carrier for loading thereon a catalyst component to purify the harmful substances present in an exhaust gas. It is known that as a material constituting such a honeycomb structure, there are used refractory particles such as silicon carbide (SiC) particles or the like.
- 15 [0003] As a specific technique related thereto, there is disclosed, in, for example, JP-A-6-182228, a porous, silicon carbide-based catalyst carrier of honeycomb structure, obtained by using, as a starting material, a silicon carbide powder having a given specific surface area and a given impurity content, molding the material into a desired shape, drying the molded material, and firing the resulting material at a temperature of 1,600 to 2,200°C.
- 20 [0004] Meanwhile, there are disclosed, in JP-A-61-26550, a process for producing a vitrifying material-containing refractory, which comprises adding a vitrifying material to an easily oxidizable material or a refractory composition containing an easily oxidizable material, mixing and kneading them together with a binder, molding the kneaded material, and open-firing the molded material in a furnace under a non-oxidative atmosphere; and, in JP-A-8-165171, a silicon carbide molded material obtained by adding, to a silicon carbide powder, an organic binder and inorganic binders of clay mineral series, glass series and lithium silicate series and molding the resulting material.
- 25 [0005] Also, in JP-A-6-182228 is introduced a process for producing a conventional porous, silicon carbide-based sintered material, which comprises adding, to silicon carbide particles as an aggregate, a binder such as vitreous flux, clay or the like, molding them, and firing the molded material at a temperature at which the binder melts.
- 30 [0006] Further, there are reported, in JP-B-61-13845 and JP-B-61-13846, the preferred average particle diameter of refractory particles, particle size distribution of refractory particles, porosity of cylindrical material, average pore diameter of cylindrical material, pore volume of cylindrical material, wall thickness of cylindrical material, etc as to a high-temperature use ceramic filter produced by molding refractory particles which consists of silica sand, a ground pottery, a metal oxide such as Al_2O_3 , TiO_2 or ZrO_2 , silicon carbide, nitride, boride, or other refractory material adjusted to a given grain size, to a porous, bottomed cylindrical material using a refractory binder such as water glass, flit, glaze or the like.
- 35 [0007] In the sintering (necking between particles) owing to the recrystallization of silicon carbide powder per se, shown in JP-A-6-182228, porosity is obtained but the silicon carbide powder per se is allowed to give rise to recrystallization; therefore, a very high firing temperature need be used which invites a high cost and, moreover, a material of high thermal expansion coefficient need be fired at a high temperature which invites a reduced yield in firing.
- 40 [0008] Meanwhile, the technique of binding a silicon carbide powder (as a raw material) with a vitreous material, shown in JP-A-61-26550 and JP-A-6-182228 uses a low firing temperature of 1,000 to 1,400°C; however, the binder once melts during the firing, making it very difficult to obtain a porous material.
- 45 [0009] Further, the filter shown in JP-B-61-13845 and JP-B-61-13846 is porous but a bottomed cylindrical material having a large wall thickness of 5 to 20 mm; therefore, it was unusable under the condition of high space velocity (SV) experienced by a filter for purification of automobile exhaust gas.
- 50 [0010] The present invention has been made in view of the above-mentioned situation of the prior art, and is intended to provide a honeycomb structure which contains refractory particles (e.g. silicon carbide particles) and yet can be produced at a relatively low firing temperature at a low cost, which has a sufficiently high porosity and a high specific surface area, and which can be suitably used, for example, as a filter for purification of automobile exhaust gas by a treatment such as plugging of through-channel at its inlet or outlet, or as a catalyst carrier even under a high SV condition.

Disclosure of the Invention

- 55 [0011] According to the present invention, there is provided a honeycomb structure having, in the axial direction, a number of through-channels separated by partition walls, which honeycomb structure contains refractory particles and a vitreous component and is porous.
- [0012] According to the present invention, there is also provided a process for producing a honeycomb structure, which comprises adding a vitrifying material and an organic binder to refractory particles as a raw material, mixing and

kneading them to obtain a readily formable bullet, extruding the readily formable bullet into a honeycomb shape, calcinating the extruded material to remove the organic binder contained therein, and then firing the calcinated material.

Best Mode for Carrying Out the Invention

[0013] The honeycomb structure of the present invention contains refractory particles and a vitreous component binding the refractory particles. Therefore, in its production, a relatively low firing temperature can be used for sintering; a low production cost is made possible; and a high yield can be obtained. The present invention is not directed to a bottomed cylindrical material of thick wall such as disclosed in JP-B-61-13845 or JP-B-61-13846 but directed to a porous honeycomb structure; accordingly, the present honeycomb structure can be used under a high SV condition, as a filter for purification of automobile exhaust gas, a catalyst carrier, or the like.

[0014] The honeycomb structure of the present invention preferably has a microstructure wherein the refractory particles are bound by the vitreous component in such a state that the particles used as a raw material for the refractory particles retain their shapes. Also, the honeycomb structure of the present invention preferably has a porosity of 30 to 90% when it is used as a filter for capturing and removing the particulate matter present in a dust-containing fluid. When the porosity of the honeycomb structure is less than 30%, the filtration rate is insufficient; when the porosity is more than 90%, the strength of the structure is insufficient. The porosity is preferably 40% or more when the present honeycomb structure is used in an application for such as for example as a filter for purification of automobile exhaust gas wherein there is a fear of pressure loss.

[0015] When the honeycomb structure of the present invention is used also as a filter, the honeycomb structure preferably has an average pore diameter determined depending upon the target substance to be filtered. For example, when the honeycomb structure is used as a diesel particulate filter (DPF) for capturing and removing the particulates contained in the exhaust gas emitted from a diesel engine, the average pore diameter is preferably set at 2 to 50 μm . When the average pore diameter is less than 2 μm , a very large increase in pressure loss appears even when the accumulation amount of particulates is small. When the average pore diameter is more than 50 μm , particulates pass through the DPF. Therefore, such average pore diameters are not preferred.

[0016] In the honeycomb structure, the thickness of the partition walls separating the through-channels (cells) is preferably 4 mil or more (102 μm or more). When the thickness of the partition walls is less than 4 mil (102 μm), the honeycomb structure has an insufficient strength. Generally in honeycomb structures, the strength has a close connection with the porosity. In the case of the present honeycomb structure, it was found out that when the thickness of the partition walls is set so as to have the following relationship with the porosity, a required strength is obtained:

$$\text{thickness of partition walls } (\mu\text{m}) \geq \text{porosity } (\%) \times 4$$

[0017] When the thickness of the partition walls is set so as to have the following relationship with the porosity, a sufficient strength is obtained:

$$\text{thickness of partition walls } (\mu\text{m}) \geq \text{porosity } (\%) \times 5$$

[0018] Meanwhile, when the present honeycomb structure is used as a filter such as DPF or the like, the thickness of the partition walls is preferably set at 50 mil or less (1,270 μm or less). When the thickness of the partition walls is more than 50 mil (1,270 μm), there are fears of filtration rate shortage and pressure loss increase. The filtration rate and pressure loss of such a filter have close connections with the porosity, and the above fears can be eliminated by setting the thickness of the partition walls so as to have the following relationship with the porosity:

$$\text{thickness of partition walls } (\mu\text{m}) \leq \text{porosity } (\%) \times 20$$

[0019] The honeycomb structure preferably has a cell density of 5 to 1,000 cells/in.² (0.7 to 155 cells/cm²). When the cell density is less than 5 cells/in.² (0.7 cells/cm²), the honeycomb structure has an insufficient strength and, when used as a filter, has an insufficient filtration area. When the cell density is more than 1,000 cells/in.² (155 cells/cm²), an increase in pressure loss is invited. Therefore, such cell densities are not preferred.

[0020] Then, description is made on the process for producing the honeycomb structure of the present invention. In producing the honeycomb structure of the present invention, first, a vitrifying material and an organic binder are added to refractory particles as a raw material, followed by mixing and kneading, to obtain a readily formable bullet.

[0021] There is no particular restriction as to the kind of the refractory particles used. However, there are preferably

used particles of Al_2O_3 , ZrO_2 , or Y_2O_3 (oxides); SiC (carbide); Si_3N_4 or AlN (nitrides); mullite; or the like. In applications such as DPF often exposed to high temperatures during the combustion of accumulated particulates, SiC or the like is preferably used for the high heat resistance.

[0022] The refractory particles as a raw material preferably have an average particle diameter of 2 to 4 times the average pore diameter of the honeycomb structure (sintered material) finally obtained in the present process. In the honeycomb structure obtained in the present process, the firing temperature is relatively low and, therefore, the particle shape and particle diameter of the refractory particles used as a raw material are almost retained even after the firing. As a result, when the above ratio is less than 2 times, the particle diameter is too small as compared to the desired pore diameter of the honeycomb structure obtained; consequently, small refractory particles are bound by a vitreous material in a thin and long shape to form large pores, and it is difficult to obtain a structure of high strength which can function as a honeycomb structure of thin walls.

[0023] When the refractory particles are, for example, SiC particles and when the SiC are recrystallization SiC conventionally used in porous honeycomb structures, the particles as a raw material for recrystallization SiC need to have, in view of the recrystallization reaction mechanism, about the same particle diameter as the desired pore diameter of the honeycomb structure obtained. In contrast, in the case of the SiC particles bound by a vitreous component, as in the honeycomb structure of the present invention, their particle diameter may be 2 times or more the pore diameter of the honeycomb structure; therefore, in order to obtain the same desired pore diameter, a raw material (SiC particles) of larger diameter (i.e. lower cost) than the raw material of recrystallization SiC can be used, resulting in a large cost merit.

[0024] When the above ratio is more than 4 times, the diameter of the refractory particles used is too large as compared with the desired pore diameter and it is difficult to obtain pores of desired diameter between the refractory particles even by packing the refractory particles closely during the molding. Further, a reduction in porosity is incurred when using the obtained honeycomb structure as a filter. Thus, such a ratio is not preferred.

[0025] The impurities contained in the refractory particles as a raw material invite a reduction in softening point of vitrifying material and have an adverse effect on the result of sintering. Therefore, the content of the impurities is preferably controlled at 5% by weight or less. The content of, in particular, alkali metals and alkaline earth metals has a large influence on the reduction in softening point and accordingly is preferably controlled at 1% by weight or less.

[0026] There is no particular restriction as to the kind of the vitrifying material as long as it melts at $1,000^\circ\text{C}$ or more and can form a vitreous material. The vitrifying material may be, for example, a material which is not vitreous when mixed with refractory particles, etc., is composed of at least one kind of oxide or the like selected from vitrifying materials such as SiO_2 , Al_2O_3 , B_2O_3 , Na_2O , Li_2O , MgO , K_2O , CaO and the like, and melts with each other and becomes a vitreous material during the firing step, or may be a flit type material which is vitreous per se.

[0027] The former material has a merit in that when composed of a plurality of oxides or the like, the melting temperature range can have a width and it is possible to avoid quick melting and viscosity reduction. The latter material has a merit in that the melting temperature range can be restricted and therefore the firing conditions can be set easily. Further, the vitrifying material useable in the present process includes even a vitrifying material containing not only a material which becomes a complete vitreous material after firing but also a material which is converted into a crystalline material (e.g. crystallized glass) through a crystallization step after melting. There are also suitably used a clay, a water glass, a glaze, etc. as long as they perform the same role.

[0028] The vitrifying material has a role of melting during firing, covering the surface of refractory particles and binding the particles. Therefore, the adequate amount of the vitrifying material used has a close connection with the surface area of the refractory particles. Here, the surface area of the refractory particles differs depending upon the shape, etc. of the refractory particles; however, since the vitrifying material melts and adheres to the refractory particles, it is generally appropriate that the surface area of the refractory particles is taken as the geometrical surface area [$S = 4\pi r^2$ (r is an average particle diameter of refractory particles)] when each refractory particle is regarded as a sphere and not taken as the BET specific surface area. By using this geometrical surface area [$S = 4\pi r^2$], "vitrifying material amount W per unit surface area of refractory particles" can be easily calculated from the following formula:

$$W = [(4/3\pi r^3 \rho_p) / (\text{weight proportion of refractory particles})] \times [(\text{weight proportion of vitrifying material}) / (4\pi r^2)]$$

(wherein r is the average diameter of refractory particles and ρ is the specific gravity of refractory particles).

[0029] In the process of the present invention, the amount of the vitrifying material added is preferably determined so that the "vitrifying material amount W per unit surface area of refractory particles" becomes 3 to 30 g/m^2 . When the

W is less than 3 g/m², the amount of the binder is insufficient and it is impossible to obtain a thin-wall structure (e.g. a honeycomb structure) having a strength sufficient for retaining its shape. When the W is more than 30 g/m², the vitreous material is present in an amount larger than necessary for appropriately binding the refractory particles; therefore, although an increased strength is obtained, there appear demerits such as reduction in porosity, reduction in average pore diameter, and the like.

[0030] The average particle diameter of the vitrifying material is preferably 50% or less of the average particle diameter of the refractory particles which are an aggregate. The vitrifying material melts upon firing, combines between its particles, and covering the surface of the refractory particles; therefore, when the particle diameter thereof is more than 50% of the particle diameter of the refractory particles, the spaces occupied by the vitrifying material particles become large voids during molding, which invites an reduction in strength; when the honeycomb structure obtained is used as a filter, a reduction in filtrability, i.e. leakage during filtration takes place.

[0031] In general, extrusion of honeycomb structure can be conducted smoothly by using a mixture of two or more kinds of material powders different in grain sizes. From this standpoint, the average particle diameter of the vitrifying material is preferably 30% or less of the average particle diameter of the refractory particles which are an aggregate.

[0032] In order to extrude the bullet smoothly, into a honeycomb shape, a readily formable bullet obtained by compounding refractory particles (an aggregate), a vitrifying material and, as necessary, a pore forming material, etc., it is preferred to add at least one kind of organic binder in order to extrude the bullet smoothly, in an amount of 2% by weight or more based on the total amount of the main raw materials (the refractory particles and the vitrifying material). However, addition of the organic binder in an amount of more than 30% by weight is not preferred because it invites too high a porosity after calcination (this leads to an insufficient strength).

[0033] The organic binder is added in an amount of preferably 4 to 20% by weight when a honeycomb structure having a partition wall thickness of 20 mil (508 μ m) or less is extruded. When the addition amount is less than 4% by weight, extrusion in such a thin wall is difficult. When the addition amount is more than 20% by weight, the extruded material is difficult to retain its shape.

[0034] When the honeycomb structure is used as a filter, a pore forming material may be added at the time of producing a readily formable bullet, in order to obtain a higher porosity. The amount of the pore forming material added is preferably 30% by weight or less based on the total amount of the main raw materials (the refractory particles and the vitrifying material). When the amount is more than 30% by weight, too high a porosity and an insufficient strength are incurred. The average particle diameter of the pore forming material is preferably 25 to 100% of the desired average pore diameter to be obtained after firing, because pores are formed at the sites where the hole-making agent has burnt and disappeared.

[0035] The above-mentioned raw materials are mixed and kneaded by an ordinary method to form a readily formable bullet, and the bullet is formed into a desired honeycomb shape by extrusion formed or the like. The formed material is calcinated to remove (debind) the organic binder contained in the formed material, followed by firing. The calcination is conducted preferably at temperatures lower than the temperature at which the vitrifying material melts. Specifically, the calcination may be carried out by keeping at a predetermined temperature between about 150 and 700°C tentatively, or by using a small temperature elevation rate of 50°C/hr or less within a predetermined temperature range.

[0036] When the calcination is carried out by keeping at a predetermined temperature tentatively, one may keep tentatively the temperature at a single level or a plurality of levels, depending upon the kind and amount of the organic binder used and; in the latter case of keeping the temperature at a plurality of the levels, the keeping time at the temperatures may be the same or different. When the calcination is conducted by using a small temperature elevation rate, the small temperature elevation rate may be used in a single temperature range or in a plurality of temperature ranges and, in the latter case, the temperature elevation rates used may be the same or different.

[0037] The atmosphere used in the calcination may be an oxidizing atmosphere. However, when a large amount of an organic binder is contained in the formed material, it may be ignited by oxygen during the calcination and thereby the formed material temperature may be increased rapidly; therefore, the calcination may preferably be conducted in an inert atmosphere (e.g. N₂ or Ar) to suppress the abnormal temperature rise of formed material. This suppression of abnormal temperature rise is important when raw materials having large thermal expansion coefficients (low thermal impact resistances) are used. When an organic binder is used in an amount of, for example, 20% by weight or more based on the total amount of the main raw materials, it is preferred to conduct calcination in the above-mentioned inert atmosphere.

[0038] Calcination and subsequent firing may be conducted as independent steps in the same furnace or in different furnaces, or may be conducted as a continuous step in the same furnace. The former operation is preferred when calcination and firing are conducted in different atmospheres; and the latter operation is preferred from the standpoint of total time of calcination and firing, running cost of furnace, etc.

[0039] The temperature employed in the firing differs depending upon the kind of the vitrifying material used but is ordinarily preferred to be 1,000 to 1,600°C. When the temperature of the firing is less than 1,000°C, the vitrifying material does not melt sufficiently and the refractory particles are not bound to each other strongly. When the temper-

ature is more than 1,600°C, the molten vitrifying material has too low a viscosity and concentrates locally at about the surface of the fired material or at the bottom of the fired material. Therefore, such firing temperatures are not preferred.

[0040] Preferably, the atmosphere used in the firing is selected depending upon the kind of the refractory particles used. When the refractory particles are those having a fear of oxidation at high temperatures, such as carbide particles (e.g. SiC), nitride particles typified by Si_3N_4 or AlN , and the like, it is preferred to use a non-oxidizing atmosphere (e.g. N_2 or Ar) at least in a temperature range where oxidation takes place.

[0041] The present invention is described in detail below by way of Examples. However, the present invention is in no way restricted to these Examples.

10 (Example 1)

[0042] There were uniformly mixed and kneaded 85 parts by weight of a SiC powder having an average particle diameter of 50.0 μm , 15 parts by weight of a vitrifying material having an average particle diameter of 10.8 μm , 6 parts by weight of methyl cellulose as an organic binder, 5 parts by weight of graphite as a pore forming material, 2.5 parts by weight of a surfactant and 24 parts by weight of water, to obtain a readily formable bullet. The bullet was extruded into a honeycomb shape having an outer diameter of 45 mm, a length of 120 mm, a partition wall thickness of 0.43 mm and a cell density of 100 cells/in.² (16 cells/cm²) using an extruder. This honeycomb extruded material was subjected to calcination for degreasing at 550°C for 3 hours in an oxidizing atmosphere, followed by firing at 1,400°C for 2.5 hours in a non-oxidizing atmosphere, to produce a SiC sintered material of porous honeycomb structure. This sintered material was measured for average pore diameter and porosity by a mercury porosimeter and further for three-point bending strength. The results are shown in Table 1. Incidentally, the three-point bending strength was calculated using the following formula:

$$\sigma = (FxS)/(4xZ)$$

(wherein σ is a three-point bending strength, F is a load, S is a lower span distance (35 mm), and Z is a sectional secondary moment).

30 (Example 2)

[0043] A sintered material was obtained by conducting the same kneading, extruding and firing as in Example 1 except that the SiC powder was changed to a SiC powder having an average particle diameter of 32.6 μm . The sintered material was measured for average pore diameter, porosity and three-point bending strength in the same manners as in Example 1. The results are shown in Table 1.

(Example 3)

[0044] A sintered material was obtained by conducting the same kneading, extruding and firing as in Example 1 except that the amounts of the SiC powder and the vitrifying material were changed to 70 parts by weight and 30 parts by weight, respectively. The sintered material was measured for average pore diameter, porosity and three-point bending strength in the same manners as in Example 1. The results are shown in Table 1.

(Example 4)

[0045] A sintered material was obtained by conducting the same kneading, extruding and firing as in Example 1 except that the SiC powder was changed to a SiC powder having an average particle diameter of 32.6 μm and the amounts of the SiC powder and the vitrifying material were changed to 65 parts by weight and 35 parts by weight, respectively. The sintered material was measured for average pore diameter, porosity and three-point bending strength in the same manners as in Example 1. The results are shown in Table 1.

(Example 5)

[0046] Honeycomb structures each having a larger diameter than that of the honeycomb structures of Examples 1 to 4 were produced. Also, honeycomb structures were produced each using a readily formable bullet containing the same organic binder in a larger amount than in Examples 1 to 4. When these honeycomb structures were calcinated for debinding in an oxidizing atmosphere in the same manner as in Examples 1 to 4, there could be obtained sintered materials having the same properties as in Examples 1 to 4, at a yield of 90% or more. When the above honeycomb

EP 1 170 270 A1

structures were calcinated in an inert atmosphere, there was no cell breakage or the like and there could be obtained good sintered materials at a zero percent defective.

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Table 1

	Av. particle diameter of SiC powder (μm)	Amount of SiC powder used (wt. parts)	Amount of vitrifying material used (wt. parts)	Av. pore diam. (μm)	Porosity (%)	Strength (kgf/mm ²)	(Av. particle diam. of SiC powder)/(av. pore diam. of sintered material)	(Amount of vitrifying material used)/(surface area of SiC powder)
Ex. 1	50.0	86	15	16.6	43.2	2.59	3.01	9.18
Ex. 2	32.6	85	15	10.3	48.4	2.28	3.17	5.98
Ex. 3	50.0	70	30	19.5	30.9	4.36	2.56	22.29
Ex. 4	32.6	65	35	13.0	38.6	5.39	2.51	18.26

[0047] As is clear from the above results, in order to obtain a honeycomb structure having an intended average pore diameter, the particle diameter of the SiC powder used as a raw material for the honeycomb structure can be selected easily. Further, the amount of the vitrifying material used also as a raw material can be determined at an appropriate level. Thus, an intended honeycomb structure can be produced at a low cost.

Industrial Applicability

[0048] As described above, the honeycomb structure of the present invention contains refractory particles such as SiC particles or the like and yet, in its production, sintering can be conducted at a relatively low temperature; therefore, its production cost can be suppressed at a low level, its yield is high, and a product of low price can be provided. Further, being porous, the present honeycomb structure can be suitably used even under a high SV condition, as a filter for purification of automobile exhaust gas, a catalyst carrier, or the like.

Claims

1. A honeycomb structure having, in the axial direction, a number of through-channels separated by partition walls, **characterized in that** honeycomb structure contains refractory particles and a vitreous component and is porous.
2. A honeycomb structure according to Claim 1, wherein the refractory particles are bound by the vitreous component in such a state that the particles used as a raw material for the refractory particles retain their shapes.
3. A honeycomb structure according to Claim 1, wherein the refractory particles are silicon carbide particles.
4. A honeycomb structure according to Claim 1, which is used as a filter for capturing and removing the particulate matter present in a dust-containing fluid.
5. A honeycomb structure according to Claim 1, which has a porosity of 30 to 90%.
6. A honeycomb structure according to Claim 1, which has an average pore diameter of 2 to 50 μm .
7. A honeycomb structure according to Claim 1, wherein the partition walls have a thickness of 102 to 1,270 μm .
8. A honeycomb structure according to Claim 1, wherein the thickness of the partition walls and the porosity of the honeycomb structure satisfy the following relationship:

$$\text{thickness of partition walls } (\mu\text{m}) \geq \text{porosity } (\%) \times 4$$

9. A honeycomb structure according to Claim 1, wherein the thickness of the partition walls and the porosity of the honeycomb structure satisfy the following relationship:

$$\text{thickness of partition walls } (\mu\text{m}) \geq \text{porosity } (\%) \times 5$$

10. A honeycomb structure according to Claim 1, wherein the thickness of the partition walls and the porosity of the honeycomb structure satisfy the following relationship:

$$\text{thickness of partition walls } (\mu\text{m}) \leq \text{porosity } (\%) \times 20$$

11. A honeycomb structure according to Claim 1, which has a through-channels density of 0.7 to 155 cells/ cm^2 .
12. A process for producing a honeycomb structure, **characterized by** adding a vitrifying material and an organic binder to refractory particles as a raw material, mixing and kneading them to obtain a readily formable bullet, forming the readily formable bullet into a honeycomb shape, calcinating the formed material to remove the organic binder contained therein, and then firing the calcinated material.

EP 1 170 270 A1

13. A process according to Claim 12, wherein the refractory particles as a raw material is silicon carbide particles.
14. A process according to Claim 12, wherein the refractory particles as a raw material has an average particle diameter of 2 to 4 times the average pore diameter of the honeycomb structure obtained finally.
- 5 15. A process according to Claim 12, wherein the refractory particles as a raw material contain impurities in an amount of 5% by weight or less.
- 10 16. A process according to Claim 12, wherein the vitrifying material contains at least one kind of oxide selected from the group consisting of SiO_2 , Al_2O_3 , B_2O_3 and Na_2O .
17. A process according to Claim 12, wherein the vitrifying material is added in an amount of 3 to 30 g per m^2 of the surface area of the refractory particles.
- 15 18. A process according to Claim 12, wherein the vitrifying material has an average particle diameter of 50% or less of the average particle diameter of the refractory particles as an aggregate.
19. A process according to Claim 12, wherein the organic binder is added in an amount of 2 to 30% by weight relative to the total amount of the refractory particles as a raw material and the vitrifying material.
- 20 20. A process according to Claim 12, wherein at the time of preparing the readily formable bullet, a pore forming material is added in an amount of 30% by weight or less relative to the total amount of the refractory particles as a raw material and the vitrifying material.
- 25 21. A process according to Claim 12, wherein the calcination of the molded material is carried out at a temperature lower than the melting temperature of the vitrifying material.
22. A process according to Claim 12, wherein the firing is carried out at a temperature between 1,000 and 1,600°C.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP01/00078

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ C04B38/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ C04B38/00-38/10, F01N 3/00-3/38		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 11-92215, A (Asahi Glass Co., Ltd.), 06 April, 1999 (06.04.99), Claim (Family: none)	1-22
Y	JP, 7-163822, A (NGK INSULATORS, LTD.), 27 June, 1995 (27.06.95), Claim & DE, 69414084, C	1-22
Y	JP, 4-187578, A (IBIDEN CO., LTD.), 06 July, 1992 (06.07.92), Claim; page 1, right column (Family: none)	1-22
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
Date of the actual completion of the international search 02 April, 2001 (02.04.01)		Date of mailing of the international search report 10 April, 2001 (10.04.01)
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HONEYCOMB STRUCTURE AND METHOD FOR MANUFACTURE THEREOF

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Equivalents: AU2548301, BR0104047, ☐ CA2362763, ID30264, ☐ US2002180117,
☐ US6716512, ☐ WO0153233
Cited Documents:

Abstract

A honeycomb structure having, in the axial direction, a number of through-channels separated by partition walls, which honeycomb structure contains refractory particles and a vitreous component and is porous. Although the honeycomb structure contains refractory particles such as silicon carbide particles or the like, it can be produced at a relatively low firing temperature; therefore, the honeycomb structure has a low production cost and a high yield and can be provided at a low price.

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(54) 【発明の名称】 ハニカム構造体及びその製造方法

(57) 【要約】

【課題】 炭化珪素粒子のような耐火性粒子を含みながらも比較的低い焼成温度で安価に製造できるとともに、十分に多孔質かつ高比表面積で、自動車排ガス浄化用のフィルターや触媒担体等として高SV条件下でも好適に使用できるハニカム構造体を提供する。

【解決手段】 隔壁により仕切られた軸方向に貫通する多数の流通孔を有するハニカム構造体であって、耐火性粒子とガラス質成分とを含み、多孔質であるハニカム構造体。

【特許請求の範囲】

【請求項1】 隔壁により仕切られた軸方向に貫通する多数の流通孔を有するハニカム構造体であって、耐火性粒子とガラス質成分とを含み、多孔質であることを特徴とするハニカム構造体。

【請求項2】 前記耐火性粒子が、その原料粒子形状を留めた状態で前記ガラス質成分により結合された構造を有する請求項1記載のハニカム構造体。

【請求項3】 前記耐火性粒子が、炭化珪素粒子である請求項1記載のハニカム構造体。

【請求項4】 含塵流体中に含まれる粒子状物質を捕集除去するフィルターとして用いられる請求項1記載のハニカム構造体。

【請求項5】 気孔率が30～90%の範囲にある請求項1記載のハニカム構造体。

【請求項6】 平均細孔径が2～50 μ mの範囲にある請求項1記載のハニカム構造体。

【請求項7】 前記隔壁の厚さが102～1270 μ mである請求項1記載のハニカム構造体。

【請求項8】 前記隔壁の厚さとハニカム構造体の気孔率とが以下の関係を満たす請求項1記載のハニカム構造体。

【数1】 隔壁の厚さ(μ m) \geq 気孔率(%) \times 4

【請求項9】 前記隔壁の厚さとハニカム構造体の気孔率とが以下の関係を満たす請求項1記載のハニカム構造体。

【数2】 隔壁の厚さ(μ m) \geq 気孔率(%) \times 5

【請求項10】 前記隔壁の厚さとハニカム構造体の気孔率とが以下の関係を満たす請求項1記載のハニカム構造体。

【数3】 隔壁の厚さ(μ m) \leq 気孔率(%) \times 20

【請求項11】 セル密度が0.7～155セル/cm²である請求項1記載のハニカム構造体。

【請求項12】 耐火性粒子原料にガラス化素材と有機バインダーとを添加し混合及び混練して得られた坯土をハニカム形状に成形し、得られた成形体を仮焼して成形体中の有機バインダーを除去した後、本焼成することを特徴とするハニカム構造体の製造方法。

【請求項13】 前記耐火性粒子原料が、炭化珪素粒子原料である請求項12記載の製造方法。

【請求項14】 前記耐火性粒子原料の平均粒子径が、最終的に得られるハニカム構造体の平均細孔径の2～4倍である請求項12記載の製造方法。

【請求項15】 前記耐火性粒子原料の不純物含有量が5重量%以下である請求項12記載の製造方法。

【請求項16】 前記ガラス化素材が、SiO₂、Al₂O₃、B₂O₃及びNa₂Oからなる群より選ばれた1種以上の酸化物を含んで構成される請求項12記載の製造方法。

【請求項17】 前記ガラス化素材の添加量が、耐火性

粒子の表面積に対し3～30g/m²である請求項12記載の製造方法。

【請求項18】 ガラス化素材の平均粒子径が、骨材である耐火性粒子の平均粒子径の50%以下である請求項12記載の製造方法。

【請求項19】 前記有機バインダーを、前記耐火性粒子原料とガラス化素材との合計量に対して、外配で2～30重量%の範囲で添加する請求項12記載の製造方法。

10 【請求項20】 前記坯土を調合する際に、造孔剤を、前記耐火性粒子原料とガラス化素材との合計量に対して、外配で30重量%以下の範囲で添加する請求項12記載の製造方法。

【請求項21】 前記成形体の仮焼を、前記ガラス化素材が溶融する温度より低い温度にて実施する請求項12記載の製造方法。

【請求項22】 前記本焼成を、1000～1600℃の温度範囲で実施する請求項12記載の製造方法。

【発明の詳細な説明】

20 【0001】

【発明の属する技術分野】 本発明は、自動車排ガス浄化用のフィルターや触媒担体等に使用されるハニカム構造体に関する。

【0002】

【従来の技術】 ディーゼルエンジン排ガスのような含塵流体中に含まれる粒子状物質を捕集除去するためのフィルター、あるいは排ガス中の有害物質を浄化する触媒成分を担持するための触媒担体として、多孔質のハニカム構造体が広く使用されている。また、このようなハニカム構造体の構成材料として、炭化珪素(SiC)粒子のような耐火性粒子を使用することが知られている。

30 【0003】 具体的な関連技術として、例えば特開平6-182228号公報には、所定の比表面積と不純物含有量を有する炭化珪素粉末を出発原料とし、これを所望の形状に成形、乾燥後、1600～2200℃の温度範囲で焼成して得られるハニカム構造の多孔質炭化珪素質触媒担体が開示されている。

【0004】 一方、特開昭61-26550号公報には、易酸化性素材、または易酸化性素材を含有する耐火組成物にガラス化素材を添加し、結合材と共に混合、混練および成形し、成形した成形体を非酸化雰囲気の中で焼成することを特徴とするガラス化素材含有耐火物の製造方法が、特開平8-165171号公報には、炭化珪素粉末に、有機バインダーと、粘土鉱物系、ガラス系、珪酸リチウム系の無機バインダーを添加して成形する炭化珪素成形体が、それぞれ開示されている。

【0005】 また、前記特開平6-182228号公報には、従来の多孔質炭化珪素質焼結体の製造方法として、骨材となる炭化珪素粒子にガラス質フラックス、あるいは粘土質などの結合材を加え成形した後、その成形

体を前記結合材が熔融する温度で焼き固めて製造する方法も紹介されている。

【0006】 更に、特公昭61-13845号公報及び特公昭61-13846号公報には、珪砂、陶磁器粉砕物、 Al_2O_3 、 TiO_2 、 ZrO_2 等の金属酸化物、炭化珪素、窒化物、硼化物あるいはその他の耐火性材料等よりなる所定粒度に整粒された耐火性粒子が、水ガラス、フリット、釉薬等の耐火性結合材で多孔質の有底筒状体に形成された高温用セラミックフィルターについて、その好適な耐火性粒子平均径、耐火性粒子粒度分布、筒状体気孔率、筒状体平均細孔径、筒状体細孔容積、筒状体隔壁肉厚等が開示されている。

【0007】

【発明が解決しようとする課題】 しかしながら、特開平6-182228号公報に示される、炭化珪素粉末自体の再結晶反応に依る焼結形態（ネッキング）は、多孔質が得られるものの、炭化珪素粉末自体に再結晶反応を起こさせるため、非常に焼成温度が高く、これがコスト高を招き、かつ、熱膨張率の高い材料を高温焼成しなければならないために、焼成歩留が低下するという問題があった。

【0008】 一方、特開昭61-26550号公報や特開平6-182228号公報に示される、原料炭化珪素粉末をガラス質で結合させる手法は、焼成温度としては1000~1400℃と低くて済むが、この時、結合材が一旦熔融状態となるため、多孔質を得ることが非常に困難であった。

【0009】 更に、特公昭61-13845号公報及び特公昭61-13846号公報に示されるフィルターは、多孔質ではあるものの、隔壁が5~20mmと厚い有底筒状体であり、自動車排ガス浄化用フィルターのような高SV（空間速度）条件下には適用できなかった。

【0010】 本発明は、このような従来の事情に鑑みてなされたものであり、炭化珪素粒子のような耐火性粒子を含みながらも比較的低い焼成温度で安価に製造できるとともに、十分に多孔質かつ高比表面積で、目封じ等の処理により自動車排ガス浄化用のフィルターとして、或いは触媒担体等として高SV条件下でも好適に使用できるハニカム構造体とその製造方法を提供することを目的とする。

【0011】

【課題を解決するための手段】 本発明によれば、隔壁により仕切られた軸方向に貫通する多数の流通孔を有するハニカム構造体であって、耐火性粒子とガラス質成分とを含み、多孔質であることを特徴とするハニカム構造体、が提供される。

【0012】 また、本発明によれば、耐火性粒子原料にガラス化素材と有機バインダーとを添加し混合及び混練して得られた坯土をハニカム形状に成形し、得られた成形体を仮焼して成形体中の有機バインダーを除去した

後、本焼成することを特徴とするハニカム構造体の製造方法、が提供される。

【0013】

【発明の実施の形態】 前記のとおり、本発明のハニカム構造体は、耐火性粒子とともにそれら耐火性粒子を結合するためのガラス質成分を含んでいるので、その製造時において比較的低い焼成温度で焼結させることができ、製造コストを抑えるとともに歩留まりを向上させることができる。また、本発明は、特公昭61-13845号公報や特公昭61-13846号公報に示されるような厚壁の有底筒状体ではなく、多孔質のハニカム構造体であるので、自動車排ガス浄化用のフィルターや触媒担体等として高SV条件下で使用できる。

【0014】 本発明のハニカム構造体は、その微構造として、前記耐火性粒子が、その原料粒子形状を留めた状態で前記ガラス質成分により結合された構造を有することが好ましい。また、本発明のハニカム構造体を、含塵流体中に含まれる粒子状物質を捕集除去するためのフィルターとして用いる場合、その気孔率を30~90%の範囲とすることが好ましい。ハニカム構造体の気孔率が30%未満では濾過速度が不足し、90%を超えると構造体としての強度が不足する。更に、自動車排ガス浄化用フィルター等の圧力損失が懸念される用途に用いる場合には、気孔率を40%以上とすることが好ましい。

【0015】 同様に本発明のハニカム構造体をフィルターとして用いる場合、ハニカム構造体の平均細孔径は、濾過する対象に応じて決定することが好ましい。例えば、ディーゼルエンジンから排出される排気ガス中に含まれるバティキュレート（DPF）として用いる場合には、平均細孔径を2~50μmの範囲とすることが好ましい。平均細孔径が2μm未満ではバティキュレートの少量堆積によっても著しく圧損が上昇し、逆に、50μmを超えるとバティキュレートの素抜けが起るため、好ましくない。

【0016】 ハニカム構造体の流通孔（セル）を仕切る隔壁の厚さは、4mil以上（102μm以上）とすることが好ましい。隔壁の厚さが4mil（102μm）未満では、構造体としての強度が不十分である。また、強度は気孔率と密接な関係にあり、本発明のハニカム構造体の場合、隔壁の厚さと気孔率とが以下の関係を満たすように隔壁の厚さを設定すれば、必要な強度が得られ、好ましいことが判明した。

【数4】 隔壁の厚さ(μm) ≥ 気孔率(%) × 4

【0017】 更に、隔壁の厚さと気孔率とが以下の関係を満たすように隔壁の厚さを設定すれば、十分な強度が得られるため、より好ましい。

【数5】 隔壁の厚さ(μm) ≥ 気孔率(%) × 5

【0018】 一方で、DPF等のフィルターとして用いる場合には、隔壁の厚さを、50mil以下（127

0 μm 以下)とすることが好ましい。隔壁の厚さが50 mil (1270 μm)を超えると、濾過速度不足や圧損上昇が懸念されるためである。なお、これについても気孔率と密接な関係があり、隔壁の厚さと気孔率とが以下の関係を満たすように隔壁の厚さを設定することによって、問題を回避することができる。

【数6】 隔壁の厚さ(μm) \leq 気孔率(%) $\times 20$

【0019】 ハニカム構造体のセル密度は、5~1000セル/平方インチ(0.7~155セル/ cm^2)の範囲とすることが好ましい。セル密度が5セル/平方インチ(0.7セル/ cm^2)未満では、ハニカム構造体として強度不足となるとともに、フィルターとして用いた場合には、濾過面積も不足する。逆に、1000セル/平方インチ(155セル/ cm^2)を超えると圧損上昇を招くため、好ましくない。

【0020】 次に、本発明のハニカム構造体の製造方法について説明する。本発明のハニカム構造体を製造するにあたっては、まず、耐火性粒子原料にガラス化素材と有機バインダーとを添加して混合及び混練し、成形用の坯土を得る。

【0021】 使用する耐火性粒子の種類は特に限定されないが、酸化物系では Al_2O_3 、 ZrO_2 、 Y_2O_3 、炭化物系では SiC 、窒化物系では Si_3N_4 、 AlN 、その他ムライト等の粒子が好適に用いられ、例えば、蓄積パティキュレート(蓄積パティキュレート)の燃焼処理時にしばしば高温に晒されるDPF等の用途には、 SiC 等が耐熱性が高く、好適に用いられる。

【0022】 耐火性粒子原料の平均粒子径は、本製造方法にて最終的に得られるハニカム構造体(焼結体)の平均細孔径の2~4倍であることが好ましい。本製造方法で得られるハニカム構造体は、焼成温度が比較的低いために耐火性粒子原料の粒子形状や粒子径が概ね焼成後まで維持される。したがって、前記比率が2倍未満であると、所望の細孔径に対して粒子径が小さ過ぎ、結果的に、小さな耐火性粒子群がガラス質で細長く結合されて大きな細孔を形成することになり、ハニカム構造体のような薄壁の構造体を維持し得る程高い強度を得ることができない。

【0023】 また、例えば耐火性粒子が SiC 粒子の場合、従来多孔質ハニカム構造体に適用されてきた再結晶 SiC が、その反応機構から、所望とする細孔径とはほぼ同等の骨材原料粒子径を必要とするのに対し、本発明のハニカム構造体のようにガラス質成分により結合された SiC 粒子は、粒子径が細孔径の2倍以上でよいので、同じ細孔径を得ようとした時に、再結晶 SiC に比べて粗い、すなわち安価な原料を使用することができ、コストメリットも大きい。

【0024】 逆に、前記比率が4倍を超える場合には、所望の細孔径に対して用いる耐火性粒子径が大き過ぎ、成形の段階で耐火性粒子を密に充填することによ

ても、その間隙に所望の細孔を得ることが困難となり、更にフィルター用途では、気孔率低下を招く点でも好ましくない。

【0025】 耐火性粒子原料中に含まれる不純物は、ガラス化素材の軟化点の降下を招き、焼結状態に影響を与えるため、その含有量を5重量%以下に抑えることが好ましい。特に、アルカリ金属、アルカリ土類金属については軟化点降下への影響が大きいので、1重量%以下に抑えることが好ましい。

【0026】 ガラス化素材は、1000℃以上で熔融してガラス質を形成するものであれば特に限定されず、例えば、耐火性粒子原料等と混合する時点ではガラス質ではなく SiO_2 、 Al_2O_3 、 B_2O_3 、 Na_2O 、 LiO 、 MgO 、 K_2O 、 CaO 等のガラス化素材の1種以上の酸化物等から構成され、焼成工程においてそれ等が熔融し合ってガラス質となる生原料系の素材でもよく、また、始めからガラス質であるフリット系の素材でもよい。

【0027】 前者には、複数種の酸化物等で構成すれば、熔融温度域に幅をもたせることができ、急激な熔融及び粘性低下を回避できるというメリットがあり、後者には、熔融温度域が限定できるために、焼成条件を設定し易いというメリットがある。更に、本発明の製造方法におけるガラス化素材には、焼成後完全にガラス質として存在するものに限らず、例えば、熔融後に結晶化工程を経ることによって得られる結晶化ガラス等、結晶質を含むものも含まれる。また、同等の役割を果たす性質のものであれば、粘土、水ガラス、釉薬なども好適に用いられる。

【0028】 ガラス化素材は、焼成中に溶けて耐火性粒子にまわりつき粒子同士を接合する役割を担うため、その適切な添加量は、耐火性粒子の表面積と密接な関わりがある。そして、この場合の耐火性粒子の表面積とは、ガラス質が熔融して覆い接着することを論じている訳であるから、粒子の形状等にも依るが、一般的には、いわゆるBET比表面積よりむしろ耐火性粒子を球体とみなした幾何学的表面積 $S = 4\pi r^2$ (r は耐火性粒子の平均粒子径)の方が適切である。この幾何学的表面積 $S = 4\pi r^2$ を用いると、「耐火性粒子単位表面積当たりのガラス素材量 W 」を、下式にて簡易的に算出することができる。

【数7】 $W = [(4/3\pi r^3 \times \rho) / (\text{耐火性粒子の重量割合})] \times [(\text{ガラス化素材の重量割合}) / (4\pi r^2)]$

(ここで、 r は耐火性粒子の平均粒径、 ρ は耐火性粒子の比重である。)

【0029】 本発明の製造方法において、ガラス化素材の添加量は、「耐火性粒子単位表面積当たりのガラス素材量 W 」が、3~30 g/m^2 となる様、設定することが好ましい。3 g/m^2 未満では、結合材が不足し

て、ハニカム構造のような薄壁の構造体を維持し得る強

度を得ることができず、逆に 30 g/m^3 を超えると、適切に耐火性粒子同士を結合し得る以上に過剰にガラス質が存在するため、強度は向上するものの、気孔率低下、平均細孔径縮小などの弊害が併発してくる。

【0030】 ガラス化素材の平均粒子径は、骨材である耐火性粒子の平均粒子径の50%以下であることが好ましい。ガラス化素材は、焼成で溶けて集合しながら耐火性粒子にまとわりつくように移動するため、その粒径が耐火性粒子の粒径の50%を超えると、成形時に同

ガラス化素材粒子が占有していた空間が大きな空隙となに残り、強度低下を招いたり、フィルターとして使用する場合には、フィルター効率低下（濾過漏れ）の原因となったりする。

【0031】 また、一般に、ハニカム構造体の押出成形時には、粒度差のある原料粉末2種以上を混合する方が得らに押し出すことができ、その観点からは、ガラス化素材の平均粒子径を、骨材である耐火性粒子の平均粒子径の30%以下にすることが好ましい。

【0032】 耐火性粒子を骨材とし、ガラス化素材及び必要に応じて造孔剤等を配合してなる坯土を、ハニカム形状に滑らかに押出成形するため、成形助剤として、1種以上の有機バインダーを、主原料（耐火性粒子原料とガラス化素材）の合計量に対し外配で2重量%以上添加することが好ましい。しかしながら、30重量%を超える添加は、仮焼後に過剰な高気孔率を招き、強度不足に至らしめるため好ましくない。

【0033】 更に、隔壁の厚さが 20 mil ($508\text{ }\mu\text{m}$) 以下のハニカム構造体に押出成形する場合には、4~20重量%の範囲で添加することが好ましい。添加量が4重量%未満では斯様な薄壁に押し出すことが難しく、逆に、20重量%を超えると、押し出し後にその形状を維持することが困難となる。

【0034】 ハニカム構造体をフィルターとして使用する場合には、気孔率を高める目的で、坯土の調合時に造孔剤を添加してもよい。造孔剤の添加量は、主原料（耐火性粒子原料とガラス化素材）の合計量に対し、外配で30重量%以下とすることが好ましい。添加量が30重量%を超えると、過度に気孔率が高くなり強度不足に至る。造孔剤の平均粒子径は、それが燃焼して抜けた跡に気孔が形成されるため、焼成後に得ようとする平均細孔径に対し、25~100%の範囲のものを使用することが好ましい。

【0035】 前記原料を常法により混合及び混練して得られた坯土を、押出成形法等により所望のハニカム形状に成形する。次いで、得られた成形体を仮焼して成形体中に含まれる有機バインダーを除去（脱脂）した後、本焼成を行う。仮焼は、ガラス化素材が溶融する温度より低い温度にて実施することが好ましい。具体的には、 $150\sim700^\circ\text{C}$ 程度の所定の温度で一旦保持してもよく、また、所定温度域で昇温速度を 50°C/hr 以下に

遅くしてもよい。

【0036】 所定の温度で一旦保持する手法については、使用した有機バインダーの種類と量により、一温度水準のみの保持でも複数温度水準での保持でもよく、更に複数温度水準で保持する場合には、互いに保持時間を同じにしても異ならせてもよい。また、昇温速度を遅くする手法についても同様に、ある一温度区域間のみ遅くしても複数区間で遅くしてもよく、更に複数区間の場合には、互いに速度を同じにしても異ならせてもよい。

【0037】 仮焼の雰囲気については、酸化雰囲気でもよいが、成形体中に有機バインダーが多く含まれる場合には、仮焼中にそれ等が酸素で激しく燃焼して成形体温度を急激に上昇せしめることがあるため、 N_2 、 Ar 等の不活性雰囲気で行うことによって、成形体の異常昇温を抑制することも好ましい手法である。この異常昇温の抑制は、熱膨張係数の大きい（熱衝撃に弱い）原料を用いた場合に重要な制御である。有機バインダーを、例えば主原料に対して20重量%（外配）以上添加した場合には、前記不活性雰囲気にて仮焼するのが好ましい。

【0038】 仮焼とそれに続く本焼成は、同一の或いは別個の炉にて、別工程として行ってもよく、また、同一炉での連続工程としてもよい。仮焼と本焼成を異なる雰囲気にて実施する場合には前者も好ましい手法であるが、総焼成時間、炉の運転コスト等の見地からは後者の手法も好ましい。

【0039】 本焼成の温度は、用いるガラス化素材によって異なるが、通常 $1000\sim1600^\circ\text{C}$ の範囲で実施することが好ましい。本焼成の実施温度が 1000°C 未満では、ガラス化素材の溶融が十分におこなないため耐火性粒子同士が強固に結合されず、逆に、 1600°C を超えると、溶融したガラス化素材の粘性が低下し過ぎて焼成体表面近傍や焼成体下部に集中する等の偏りが生じるため好ましくない。

【0040】 また、本焼成の雰囲気については、耐火性粒子の種類によって選択することが好ましく、例えば、 SiC をはじめとする炭化物の粒子、 Si_3N_4 、 AlN に代表される窒化物の粒子等、高温での酸化が懸念されるものについては、少なくとも酸化が始まる温度以上の温度域においては、 N_2 、 Ar 等の非酸化雰囲気とすることが好ましい。

【0041】

【実施例】 以下、本発明を実施例に基づいて更に詳細に説明するが、本発明はこれらの実施例に限定されるものではない。

【0042】（実施例1）平均粒径 $50.0\text{ }\mu\text{m}$ の SiC 原料粉末85重量部、平均粒径 $10.8\text{ }\mu\text{m}$ のガラス化素材15重量部、有機バインダーとしてメチルセルロース6重量部、造孔剤としてグラファイト5重量部、界面活性剤2.5重量部、及び水24重量部を均一に混合及び混練して得た坯土を、押し出し成形機にて外径 45 m

m、長さ120mm、隔壁厚さ0.43mm、セル密度100セル/平方インチ(16セル/cm²)のハニカム形状に成形した。このハニカム成形体を酸化雰囲気において550℃で3時間、脱脂のため仮焼を行った後、非酸化雰囲気において1400℃で2.5時間の焼成を行い、多孔質でハニカム構造の炭化珪素焼結体を作製した。この焼結体について、水銀 porosimeter にて平均細孔径と気孔率、更に3点曲げ強度を測定し、その結果を表1に示した。なお、3点曲げ強度は下記計算式を用いて算出した。

$$[\text{数}8] \sigma = (F \times S) / (4 \times Z)$$

(ここで、 σ は3点曲げ強度、Fは荷重、Sは下部スパン間隔(35mm)、Zは断面2次モーメントである。)

【0043】(実施例2) 平均粒径32.6 μ mのSiC原料粉末を用いた以外は、前記実施例1と同様に混練、成形及び焼成を行って焼結体を得た。得られた焼結体について、前記実施例1と同様に平均細孔径、気孔率及び3点曲げ強度を測定し、その結果を表1に示した。

【0044】(実施例3) SiC原料粉末を70重量部、ガラス化素材を30重量部とした以外は、前記実施例1と同様に混練、成形及び焼成を行って焼結体を得

10

*た。得られた焼結体について、前記実施例1と同様に平均細孔径、気孔率及び3点曲げ強度を測定し、その結果を表1に示した。

【0045】(実施例4) 平均粒径32.6 μ mのSiC原料粉末を用い、SiC原料粉末を65重量部、ガラス化素材を35重量部とした以外は、前記実施例1と同様に混練、成形及び焼成を行って焼結体を得た。得られた焼結体について、前記実施例1と同様に平均細孔径、気孔率及び3点曲げ強度を測定し、その結果を表1に示した。

【0046】(実施例5) 前記実施例1~4より大径のハニカム構造体を作製した場合、もしくは有機バインダーをより多く含んだ坯土を用いてハニカム構造体を作製した場合、前記実施例1~4と同様に酸化雰囲気下で脱脂のための仮焼を行っても、歩留まり90%以上に同様の特性の焼結体を得る事ができたが、不活性雰囲気下で仮焼を行うと、セル切れ等の不具合が発生すること無く、不良率0%で良好な焼結体を得ることが出来た。

【0047】

【表1】

	SiC粉末の 平均粒径(μ m)	SiC粉末の 配合量(重量部)	ガラス化素材の 配合量(重量部)	平均細孔径 (μ m)	気孔率 (%)	強度 (kgf/mm ²)	SiC粉末平均粒径 / 焼結体平均細孔径	ガラス化素材添加量 / SiC粉末表面積
実施例1	50.0	85	15	16.6	43.2	2.59	3.01	9.18
実施例2	32.6	85	15	10.3	48.4	2.28	3.17	5.98
実施例3	50.0	70	30	19.5	30.9	4.36	2.56	22.29
実施例4	32.6	65	35	18.0	38.6	5.39	2.51	18.26

【0048】 これらの結果から、必要とする平均細孔径のハニカム構造体を得るために原料SiC粉末の粒径を容易に選択することができる。また、ガラス化素材の添加量についても過不足なく設定でき、要求されるハニカム構造体を安価に製造することができる。

【0049】

【発明の効果】 以上説明したように、本発明のハニカ

※ ム構造体は、炭化珪素粒子等の耐火性粒子を含みながらも、その製造時において比較的低い焼成温度で焼結させることができるので、製造コストを抑えるとともに歩留まりも向上し、安価に提供することができる。また、多孔質のハニカム構造体であるので、自動車排ガス浄化用のフィルターや触媒担体等として高SV条件下でも好適に使用できる。

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